atoms were assigned u values of 0.07 Å^{-3}. Scattering factors for hydrogen were obtained from Stewart et al.[22] and for other atoms were taken from ref 23. Anomalous dispersion terms were applied to the scattering of Fe and P. The largest peak on a final difference electron density map was ±0.5 e Å^{-3}. Final positional and thermal parameters for non-hydrogen atoms are given in Table VI.

Collection and Reduction of X-ray Data for [PPN][10]. An amber crystal, obtained from a (CH$_2$)$_4$O/C$_2$H$_5$)$_2$O solution, was mounted with epoxy on a thin glass fiber on a modified Huber diffractometer. Unit cell parameters were determined from a least-squares fit of 25 accurately centered reflections (9.5° < 2θ < 16.4°). These dimensions and other parameters, including conditions of data collection, are summarized in Table IV. Data were collected at 25 °C in the θ–2θ scan mode. Three intense reflections, (2,-1,4), (0,3,3), and (3,1,-3), were monitored every 97 reflections to check stability. Intensities of these reflections decayed less than 1% with a maximum fluctuation of ±4.7% during the course of the experiment (55.2 h). Of the 5761 unique reflections measured, 3272 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects. Programs used include locally modified versions of the programs listed in the reference section.[21]

Solution and Refinement of the Structure of [PPN][10]. Atoms were located by use of the heavy-atom method. All calculations were performed on the VAX 3100 crystallographic computer. All phenyl hydrogens were included in calculated positions as members of rigid groups, C–H = 1.0 Å, angles = 120°. All methyl hydrogens were included in calculated positions, C–H = 1.0 Å, H–C–H = 109.5°. All carboranyl hydrogens were kept in located positions. Hydrogen atoms were assigned u values based on those of the attached atoms. Scattering factors for hydrogen were obtained from Stewart et al.[22] and for other atoms were taken from ref 23. Anomalous dispersion terms were applied to the scattering of Fe and P. The largest peak on a final difference electron density map was 0.6 e Å^{-3} and was located near a phenyl ring. Final positional and thermal parameters for nonhydrogen atoms are given in Table VII.

Supplementary Material Available: Tables of positional and thermal parameters, anisotropic thermal parameters, and interatomic distances and angles (29 pages); listings of observed and calculated structure factors (70 pages). Ordering information is given on any current masthead page.

Synthesis and Kinetics of Decomposition of Tungsten(VI) and Molybdenum(VI) 2-Oxametallacyclobutane Complexes and the X-ray Structure of *trans*-Mo[CH(*t*-Bu)CH(C$_6$F$_5$)O](NAr)(O-*t*-Bu)$_2$

Guillermo C. Bazan, Richard R. Schrock,* and Marie B. O'Regan

Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

2-Oxametallacyclobutane complexes (M = Mo (**2a**), W (**2b**)) can be prepared by adding pentafluorobenzaldehyde to M(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (M = Mo (**1a**), W (**1b**)). Two isomers are observed for **2a** and **2b** that contain *t*-Bu and Ph$_F$ substituents trans or cis to one another (the trans isomer predominating) and that decompose to give *trans*- or *cis*-Ph$_F$CH=CH(*t*-Bu), respectively. An X-ray structure of the major isomer of **2a** (**2a-trans**) showed it to be a square pyramid containing an apical imido ligand and pseudoequatorial α-*t*-Bu and β-Ph$_F$ groups in a slightly puckered MoOC$_2$ ring. It is proposed that cis isomers of **2** also contain a pseudoequatorial α-*t*-Bu group. At 25 °C **2a-trans** decomposes twice as rapidly as **2b-trans**, and at 5.0 °C **2b-cis** decomposes ~25 times more rapidly than **2b-trans**. These findings are all consistent with square-pyramidal 2-oxametallacyclobutane complexes being more stable when they contain trans α and β substituents, when electron-withdrawing substituents are present on the ring, and when a bulky substituent is present in the pseudoequatorial α position. These results are discussed in relation to findings concerning analogous MC$_3$ metallacyclobutane complexes.

Introduction

2-Oxametallacyclobutane (metallaoxetane) complexes are plausible intermediates in transition-metal-catalyzed olefin epoxidation reactions[1] and Wittig-like reactions between high oxidation state alkylidene complexes and the carbonyl functionality.[2,3] However, examples usually can be prepared only by indirect methods.[4] An exception in

(1) (a) Collman, J. P.; Brauman, J. L.; Meunier, B.; Hayashi, T.; Kodadek, T.; Raybuck, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 2000. (b) Groves, J. T.; Avaria-Neisser, G. E.; Fish, K. M.; Imachi, M.; Kuczkowski, R. L. *J. Am. Chem. Soc* **1986**, *108*, 3837. (c) Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1977**, *99*, 3120. (d) Milstein, D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 3773. (e) Alper, H.; Arzoumanian, H.; Petrignani, J.-P.; Saldana-Maldonado, M. *J. Chem. Soc., Chem. Commun.* **1985**, *340*. (f) Girardet, M.; Meunier, B. *Tetrahedron Lett.* **1987**, *2955*. (g) Mock, W. L.; Bieniarz, C. *Organometallics* **1985**, *4*, 1917. (h) Walba, D. M.; DePuy, C. H.; Grabowski, J. J.; Bierbaum, V. M. *Organometallics* **1984**, *3*, 498.

(2) (a) Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399. (b) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *101*, 3611. (c) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270. (d) Buchwald, S. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 5490. (e) Aguero, A.; Kress, J.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, *531*.

(3) (a) 3-Oxaplatinacyclobutane complexes have been reported.[3b] So far there is no evidence that 3-heteroatom metallacycles are formed in reactions between alkylidene complexes and the carbonyl function. (b) Hoover, J. F.; Stryker, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 6466.

the former category is the synthesis of an oxairidacyclobutane complex from a reaction between a cyclooctadiene complex and oxygen.[5] Two exceptions in the latter category are β-alkylidenetitana-2-oxacyclobutane complexes prepared by adding ketenes to "TiCp₂(CH₂)"[6] and oxatantalacyclobutane complexes prepared by adding aldehydes to TaCp*₂Me(CH₂).[7] Both types are relatively stable, the titanium species perhaps in part because of the nature of the olefin (an allene) that is generated when a metallacycle cleaves to give "TiCp₂(O)." Few X-ray structures of 2-oxametallacycles have been reported.[4a,h,5,7]

We have shown that metallacyclobutane complexes are intermediates in reactions between olefins and alkylidene complexes of the type M(CH-*t*-Bu)(NAr)(OR)₂ (M = Mo, W; Ar = 2,6-C₆H₃-*i*-Pr₂)[8] and that in some cases they can be isolated and structurally characterized. Square-pyramidal metallacycles form when OR = O-*t*-Bu and are much more stable than trigonal-bipyramidal metallacycles, which form when OR is more electron-withdrawing.[9] *tert*-Butoxide complexes are useful for the living ring-opening metathesis reactions of norbornenes and disubstituted norbornadienes.[10] Recent results suggest that SP metallacycles containing *tert*-butoxide ligands are *more* stable when a bulky group such as a *tert*-butyl group is in the pseudoequatorial α position or when electron-withdrawing substituents are present on the metallacyclic ring.[11] Since Wittig-like reactions with *tert*-butoxide complexes have been used routinely to cleave the polymer or oligomer from the metal, we felt that if there is a close similarity between reactions of olefins with alkylidene complexes and reactions of organic carbonyl groups with alkylidene complexes, it may be possible to stabilize the observe an intermediate 2-oxametallacyclobutane complex prepared by treating M(CH-*t*-Bu)(NAr)(O-*t*-Bu)₂ with the appropriate aldehyde. This has now been accomplished, and the results are reported here. Kinetic and mechanistic studies confirm that these 2-oxametallacyclobutane complexes and metallacyclobutane complexes are indeed closely related.

Results

Two aldehydes that have been used routinely to cleave polymers from Mo or W in living polymers are pivaldehyde and benzaldehyde.[10,11] In general some *cis*-olefin product

(4) See, for example: (a) Schlodder, R.; Ibers, J. A.; Lenarda, M.; Graziani, M. *J. Am. Chem. Soc.* **1974**, *96*, 6893. (b) Lenarda, M.; Ros, R.; Traverso, O.; Pitts, W. D.; Bradley, W. H.; Graziani, M. *Inorg. Chem.* **1977**, *16*, 3178. (c) Klein, D. P.; Hayes, J. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 3704. (d) Bennett, C. R.; Bradley, D. C. *J. Chem. Soc., Chem. Commun.* **1974**, 29. (e) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2991. (f) Miyashita, A.; Ishida, J.; Nohira, H. *Tetrahedron Lett.* **1986**, 2127. (g) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 3234. (h) Zlota, A. A.; Frolow, F.; Milstein, D. *J. Am. Chem. Soc.* **1990**, *112*, 6411. (i) Lenarda, M.; Pahor, N. G.; Calligaris, M.; Graziani, M.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1978**, 279.

(5) Day, V. W.; Klemperer, W. G.; Lockledge, S. P.; Main, D. *J. J. Am. Chem. Soc.* **1990**, *112*, 2031.

(6) Ho, S. C.; Hentges, S.; Grubbs, R. H. *Organometallics* **1988**, *7*, 780.

(7) Whinnery, L. L., Jr.; Bercaw, J. E. Presented at the 196th National Meeting of the American Chemical Society, Los Angeles, CA, Sept 25–30, 1988; Abstract No. 160

(8) (a) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875. (b) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423. (c) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L. Y.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Krüger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262.

(9) Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R. *Organometallics* **1990**, *9*, 2535.

(10) Schrock, R. R. *Acc. Chem. Res.* **1990**, *24*, 158.

(11) Bazan, G.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378.
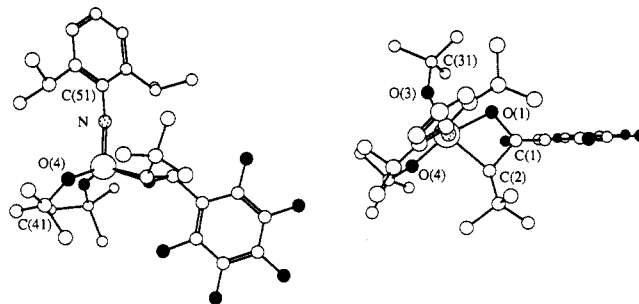
Figure 1. Two views of 2a-trans. The right structure is obtained by rotating the left structure 90° toward the viewer.

is formed in reactions involving living (propagating) alkylidenes, while *trans*-olefin is formed in reactions involving neopentylidene complexes. For example, pivaldehyde reacts smoothly with M(CH-*t*-Bu)(NAr)(O-*t*-Bu)₂ (M = Mo (1a), W (1b)) to yield exclusively *trans*-di-*tert*-butylethylene (eq 1). The reaction is fast and quantitative


M = Mo (1a) or W (1b)
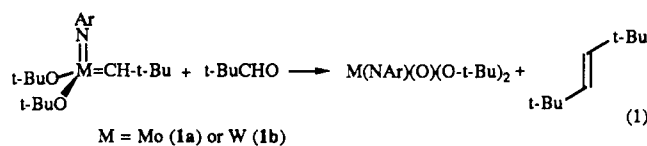
by ¹H NMR spectroscopy. M(O)(NAr)(O-*t*-Bu)₂ complexes have not yet been isolated in pure form, since they appear to disproportionate to (inter alia) M(NAr)₂(O-*t*-Bu)₂. Addition of benzaldehyde to 1 proceeds similarly except that some *cis*-PhCH=CH(*t*-Bu) is formed (2%) when M = W. No intermediates have been observed by ¹H NMR spectroscopy in these reactions at room or low temperature.

Analogous reactions between 1 and pentafluorobenzaldehyde (Ph_FCHO) require up to 3 h (eq 2). Inspection

M = Mo (1a) or W (1b)   96 % trans (M = Mo)
74 % trans (M = W)
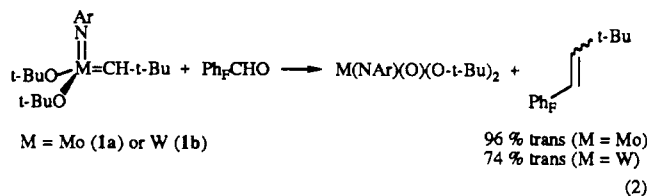
of the reaction involving 1a in C₆D₆ by ¹H NMR spectroscopy immediately after addition of C₆F₅CHO shows that two intermediates form rapidly in high yield and only relatively slowly decompose to give the observed olefins. They are proposed to be 2-oxametallacyclobutane precursors to those olefins. Since both 1a and 1b contain a *syn*-neopentylidene ligand (that with the *tert*-butyl group pointing toward the imido ligand),[8a,c] the major intermediate is proposed to contain the α-*tert*-butyl and β-Ph_F groups in pseudoequatorial positions in a bent metallacyclobutane ring (eq 3). This proposal is consistent with

M = Mo (2a) or W (2b)
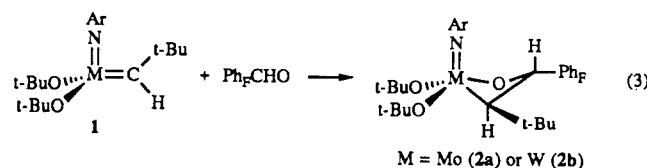
the fact that 2a-*trans* comprises 94% of the mixture and 2b-trans comprises 74% of the mixture, percentages that match the amount of *trans*-Ph_FCH=CH(*t*-Bu) ultimately formed in each case. Proton and carbon NMR spectra of 2a-trans and 2b-trans are reminiscent of those for square-pyramidal metallacyclobutane complexes that result upon addition of olefins to these same alkylidene

Table I. Selected Intramolecular Distances (Å) and Angles (deg) Involving the Non-Hydrogen Atoms in *trans*-Mo[CH(t-Bu)CH(Ph$_F$)O](NAr)(O-t-Bu)$_2$ (2a-trans)

Mo–N	1.722 (3)	Mo–C(2)	2.196 (4)
Mo–O(1)	1.995 (3)	C(1)–C(2)	1.537 (6)
Mo–O(3)	1.860 (3)	C(1)–O(1)	1.428 (5)
Mo–O(4)	1.882 (3)		
Mo–N–C(51)	167.2 (3)	O(3)–Mo–O(4)	101.3 (1)
Mo–O(3)–C(31)	148.9 (3)	O(3)–Mo–C(2)	93.2 (1)
Mo–O(4)–C(41)	148.7 (3)	O(1)–Mo–N	104.9 (1)
Mo–C(2)–C(1)	88.9 (2)	O(3)–Mo–N	106.4 (1)
Mo–O(1)–C(1)	100.5 (2)	O(4)–Mo–N	111.1 (2)
O(1)–C(1)–C(2)	99.9 (3)	C(2)–Mo–N	99.4 (2)
O(1)–Mo–C(2)	65.4 (1)	O(3)–Mo–O(1)	144.4 (1)
O(1)–Mo–O(4)	82.4 (1)	O(4)–Mo–C(2)	140.4 (1)

complexes.[9,12] For example, in 2a-trans the α- and β-proton resonances appear at 2.45 and 6.62 ppm, and the α- and β-carbon resonances at 69.98 and 72.53 ppm. The minor isomer (6%; 2a-cis) has a similar spectrum with α- and β-proton resonances at 2.64 and 6.86 ppm. We are confident that the structure of 2a-trans is as depicted in eq 3 on the basis of the X-ray results reported below but cannot be certain that 2a-cis also contains a pseudoequatorial α-*tert*-butyl group, i.e, that it also is formed from *syn*-Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$. Conceivably it could be formed from *anti*-Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$. We favor the proposal that it is formed from *syn*-Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$.

Crystals of pure 2a-trans suitable for X-ray analysis were obtained at –30 °C from octane. The results of a low-temperature X-ray analysis are shown in Figure 1. Relevant bond distances and angles are listed in Table I. The imido ligand occupies the apical position with the oxametallacycle ring and the two *tert*-butoxide ligands located in the basal plane; angles between the axial and basal ligands vary from 99.4 (2) to 111.1 (2)°. The Mo–N–C(51) angle of 167.2 (3)° is fairly typical of diisopropylphenylimido ligands in high oxidation state complexes, in which the metal is relatively electron-deficient and some π bonding between the imido nitrogen atom and the metal is likely.[8–12] The phenyl group of the imido ligand is aligned so that its plane approximately contains the Mo–O(4) and Mo–O(1) bonds, an orientation that minimizes steric interactions between the *tert*-butyl group on the ring and the isopropyl groups on the imido ligand. The *tert*-butoxide ligand that contains C(41) consequently is turned away from the imido ligand's isopropyl group. The other *tert*-butoxide ligand is also turned away from the imido ligand, even though there is no obvious intramolecular steric reason for it to do so. (The α-*tert*-butyl group in a neighboring molecule appears most likely to induce this orientation.) The Mo–O(3) bond length (1.860 (3) Å) and Mo–O(4) bond length (1.882 (3) Å) and the large Mo–O–C angles (Mo–O(3)–C(31) = 148.9 (3)° and Mo–O(4)–C(41) = 148.7 (3)° are both typical of alkoxide ligands in complexes of this type in which there is some π bonding between the metal and the alkoxide oxygen atom. The MoOC$_2$ ring is slightly puckered (21.3°) with the pentafluorophenyl and *tert*-butyl groups consequently in positions that are approximately halfway between equatorial and axial. The Mo–O(1) bond length (1.995 (3) Å) is consistent with a Mo–O single bond in which there is little π bonding between Mo and O, while the C(1)–O(1) bond length (1.428 (5) Å) is what one would expect on the basis of the structures of other 2-oxametallacyclobutane complexes and the structures of analogous all-carbon square-
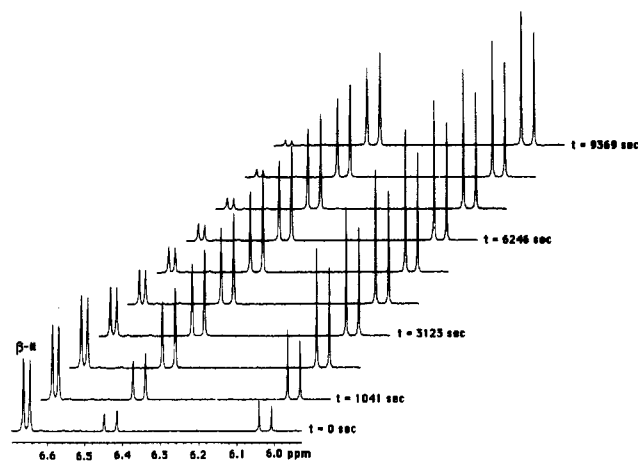
Figure 2. Representative spectra used to calculate the rate of decomposition of 2a-trans at 25 °C. (Two additional spectra were acquired between each one shown.)

Table II. Rate Constants and Kinetic Parameters for Decomposition of 2-Oxametallacycles

metallacycle	T, °C	k, 10^{-4} s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
2a-trans	35.1	6.71	17.5	–16
	30.0	4.72		
	25.0	2.52		
	15.1	0.89		
2b-trans	35.1	3.82	21.0	–7
	25.1	1.11		
	15.0	0.33		
	5.0	0.076 (calcd)		
2b-cis	5.0	1.9		

pyramidal tungstacycles (see Discussion).

The decomposition of pure 2a-trans to yield *trans*-Ph$_F$CH=CH(*t*-Bu) takes place quantitatively versus an internal standard. No *cis*-Ph$_F$CH=CH(*t*-Bu) is observed. The decomposition of 2a-trans can be followed by observing the decrease in the resonance for the β proton in the MoOC$_2$ ring and/or the rate of appearance of *trans*-Ph$_F$CH=CH(*t*-Bu) (Figure 2). The reaction is cleanly first order with $\Delta H^{\ddagger}$ = 17.5 (9) kcal mol^{-1} and $\Delta S^{\ddagger}$ = –16 (3) eu over a temperature range of ~20 °C (Table II). The rate of decomposition of 2a-trans in mixtures of 2a-trans and 2a-cis is the same as for pure 2a-trans, and as mentioned earlier, the amount of *trans*-Ph$_F$CH=CH(*t*-Bu) that is formed is within experimental error equal to the amount of 2a-trans in the mixture. The rate of decomposition of 2a-cis could not be measured because of the small amount that is present. Once 2a-cis disappears from the mixture, no more *cis*-Ph$_F$CH=CH(*t*-Bu) is formed. All these data suggest that 2a-trans decomposes to *trans*-Ph$_F$CH=CH-(*t*-Bu) and 2a-cis to *cis*-Ph$_F$CH=CH(t-Bu) without a significant amount of Ph$_F$CHO being lost from the metallacyclic ring of either isomer.

Mixtures of 2b-trans (~75%) and 2b-cis (~25%) can be prepared at low temperature. Unfortunately, pure 2b-trans or 2b-cis so far has not been induced to crystallize from the mixtures, and so their decompositions were studied in situ. The characteristics of their decomposition were found to be the same as those for mixtures of 2a-trans and 2a-cis with activation parameters for 2b-trans of $\Delta H^{\ddagger}$ = 21.5 (6) kcal and $\Delta S^{\ddagger}$ = –7 (2) eu over a temperature range of ~20 °C. In this case the decomposition of 2b-cis could be determined; at 5.0 °C, k = 1.9 × 10^{-4} s^{-1}. Comparison with the calculated rate of decomposition of 2b-trans at that temperature (7.6 × 10^{-6} s^{-1}) suggests that 2b-cis decomposes approximately 25 times faster than

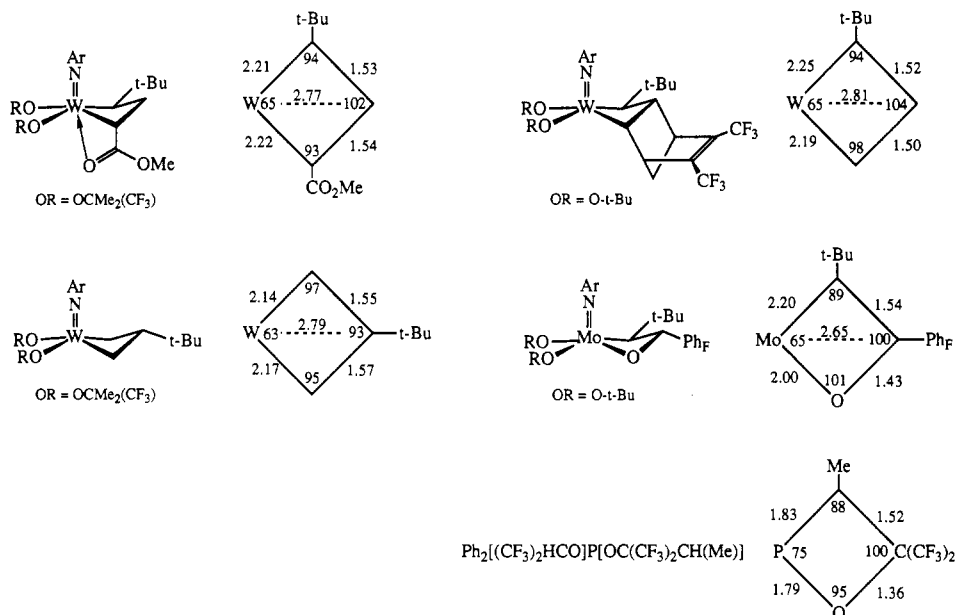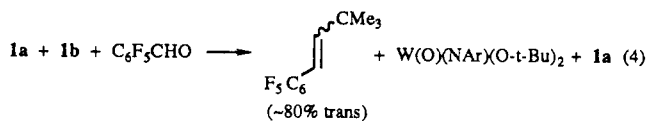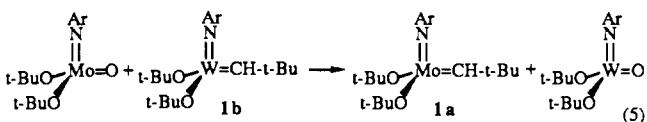(12) Feldman, J.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 2266.

Figure 3. Comparison of bond lengths and angles in the metallacyclic rings in three tungstacyclobutane complexes and an oxaphosphetane with those in the MoC_2O ring in *trans*-Mo[CH(*t*-Bu)CH(Ph$_F$)O](NAr)(O-*t*-Bu)$_2$.

2b-trans. A comparison of the decomposition of **2b**-trans with that of **2a**-trans leads to the conclusion that *trans*-molybdacycles decompose approximately twice as fast as *trans*-tungstacycles at 25 °C.

The result of a reaction between a 1:1 mixture of **1a** and **1b** and 1 equiv of C_6F_5CHO at 25 °C is shown in eq 4. The

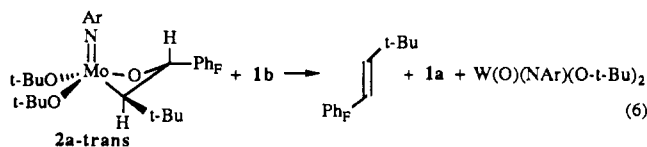$$\text{1a + 1b + } C_6F_5CHO \longrightarrow \underset{\underset{(\sim 80\% \text{ trans})}{F_5C_6}}{\overset{CMe_3}{\text{⟋}}} + \text{ W(O)(NAr)(O-}t\text{-Bu)}_2 + \text{ 1a} \quad (4)$$

percentage *trans*-Ph$_F$CH=CH(*t*-Bu) that is produced is inconsistent with what superficially appears to be a selective reaction between **1b** and Ph$_F$CHO. Therefore, the question arises as to whether Mo(O)(NAr)(O-*t*-Bu)$_2$ is stable in the presence of **1b**. The result shown in eq 5—Mo(O)(NAr)(O-*t*-Bu)$_2$ was generated in situ from Mo-

$$\underset{t\text{-BuO}}{\overset{\overset{Ar}{\overset{N}{\|}}}{\text{Mo=O}}} + \underset{t\text{-BuO}}{\overset{\overset{Ar}{\overset{N}{\|}}}{\text{W=CH-}t\text{-Bu}}} \longrightarrow \underset{t\text{-BuO}}{\overset{\overset{Ar}{\overset{N}{\|}}}{\text{Mo=CH-}t\text{-Bu}}} + \underset{t\text{-BuO}}{\overset{\overset{Ar}{\overset{N}{\|}}}{\text{W=O}}} \quad (5)$$

(CHCMe$_2$Ph)(NAr)(O-*t*-Bu)$_2$ and 1 equiv of benzaldehyde—suggests that it is not. At 25 °C the oxo ligand on Mo exchanges quantitatively with the neopentylidene ligand on W, probably via a dimeric intermediate that contains bridging oxo and bridging neopentylidene ligands. The reaction shown in eq 4 can be explained if *both* Mo-(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ react with Ph$_F$CHO, but W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ reacts approximately three times faster than Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$.

The result shown in eq 6 can be explained on the basis of the findings so far; **2a**-trans decomposes quantitatively

$$\underset{\underset{\text{2a-trans}}{t\text{-BuO}}}{\overset{\overset{\overset{Ar}{\overset{N}{\|}}}{}}{\text{Mo}}} \overset{H}{\underset{H}{\text{—O}}}\text{—Ph}_F + \text{1b} \longrightarrow \overset{t\text{-Bu}}{\text{⟋}} + \text{1a} + \text{W(O)(NAr)(O-}t\text{-Bu)}_2 \quad (6)$$

to Mo(O)(NAr)(O-*t*-Bu)$_2$ and *trans*-Ph$_F$CH=CH(t-Bu) and Mo(O)(NAr)(O-*t*-Bu)$_2$ then reacts quantitatively with

1b. Note that no *cis*-Ph$_F$CH=CH(*t*-Bu) is formed (not detectable by 500-MHz NMR), as one would expect if some Ph$_F$CHO were lost from **2a**-trans and would then react three times faster with **1b** than it would back-react with **1a.** If we propose that 1% *cis*-Ph$_F$CH=CH(*t*-Bu) could have been observed, we can then estimate that no more than ~5% Ph$_F$CHO could have been lost from **2a**-trans.

Discussion

It is informative to compare the ring structure in **2a**-trans to that in three published structures of square-pyramidal tungstacyclobutane complexes (Figure 3). The bond lengths and angles in the slightly puckered rings are remarkably similar, as are the angles at the metal (average 65°), C$_\alpha$ (average 95°), and C$_\beta$ (average 100°). The Mo–O bond (2.00 Å) and C–O bond (1.43 Å) are shorter than analogous W–C$_\alpha$ and C$_\alpha$–C$_\beta$ bonds, respectively, as one would expect on the basis of the greater electronegativity and slightly smaller size of oxygen versus carbon, but there are no grounds for claiming that the MoC_2O ring is any less symmetric than the WC_3 rings. We are forced to conclude that the 2-oxametallacycles are closely related structurally to the all-carbon tungstacycles and that perhaps the mechanism of formation and decomposition of 2-oxametallacycles is also closely related to the mechanism of formation and decomposition of all-carbon metallacycles.

The 2-oxametallacycle closest to that described here whose structure is known is Cp*$_2$Ta[OC(Ph)CH$_2$](CH$_3$).[7] The internal angles and bond distances in the slightly puckered TaC$_2$O ring are virtually identical with those in **2a**-trans. This fact is further evidence that the MoC_2O ring in **2a**-trans is not unusual in any way.

There are several features of MC_3 complexes of the square-pyramidal type that are worth highlighting. We already have mentioned two features in particular, the stability of metallacycles that contain electron-withdrawing substituents and the stability of metallacycles that contain a pseudoequatorial α-*tert*-butyl group. As far as decomposition of MC_3 complexes is concerned, we have postulated that the incipient olefin in the ring must be drawn toward the metal and must leave the coordination sphere only after binding to the metal to a significant degree,

probably via a metallacycle that has never, and may never, be observed, e.g., one that contains an axial/equatorial ring and an equatorial imido ligand.[9] This proposal is consistent with the view that the olefin adds to the metal, probably in an axial position, in order to form a metallacyclic ring, and with the fact that ΔS^* is usually substantially negative for loss of olefin from the ring ($\sim$-15 eu) in complexes of this type.[9,11] It is proposed that the presence of a *tert*-butyl group in the pseudoequatorial α position stabilizes the metallacycle primarily for steric reasons; i.e., the metallacycle cannot rearrange as readily to the required intermediate from which an olefin can be lost, and it is more difficult to lose the olefin that contains a bulky α substituent. If the energetics of olefin binding contribute to a significant degree to transition-state energies, then an olefin that contains a bulky substituent would bind more poorly in the transition state and the metallacycle would be stabilized. Likewise an olefin with an electron-withdrawing substituent also would bind relatively poorly to a relatively electropositive metal center, and the metallacycle again would be stabilized. The fact that **2a** and **2b** are relatively stable is good evidence that these principles extend to 2-oxametallacycles also. The importance of ground-state electronic effects is not known, but in a carbon system that is likely to be polarized M-$(\delta^+)C_\alpha(\delta^-)C_\beta(\delta^+)$, the presence of an electron-donating substituent on the α-carbon atom and an electron-withdrawing substituent on the β-carbon atom would appear to raise the ground-state energy rather than lower it. Note that the values for ΔS^* are not of the highest accuracy (temperature range $\sim$20 °C) and so a detailed discussion of differences in ΔS^* is not justified at this time.

Two findings reported here do not yet have counterparts on MC_3 chemistry. One is that an oxamolybdacycle rearranges more rapidly than an oxatungstacycle by a factor of 2. So far we have only been able to speculate that MoC_3 complexes rearrange more rapidly than WC_3 complexes, and this fact plus the documented slower rate of formation of molybdacycles are the main reasons why they are much less common than tungstacycles.[11] Second, we have shown that a *cis*-2-oxametallacycle (presumably that formed from the *syn*-alkylidene complex) rearranges $\sim$25 times more rapidly than a *trans*-2-oxametallacycle. No *cis*-MC_3 species has ever been observed in systems of this type (if a trans analogue can form), a fact that is consistent with accumulating evidence that *cis*-metallacyclobutane complexes rearrange much more readily than *trans*-metallacycles.[13] (*cis*-Metallacycles must be present in living ROMP reactions, since a significant percentage of the double bonds in the polymer chain of (e.g.) polynorbornene are cis.[10,13,14]) The findings reported here could be used as evidence that this proposal is correct.

It is perhaps important to note that electron-withdrawing groups also stabilize oxaphosphetane complexes; e.g., $Ph_2[(CF_3)_2HCO]P[OC(CF_3)_2CH(Me)]$[15] is stable up to 150 °C. The ring distances in the oxaphosphetane and **2a**-trans (Figure 3) are virtually identical after the larger radius of Mo relative to P is taken into account. The trend in the cis/trans distribution of olefins in the ylide reaction (more reactive ylides tend to yield more *cis*-olefin) follows that

in the tungsten and molybdenum alkylidene reactions presented here (**1b** also yields more *cis*-olefin than **1a**). In all systems (P, Mo, W) the isolated cis-substituted rings break up faster than trans-substituted rings. It should be noted that since oxaphosphetanes are not accepted as intermediates in all Wittig reactions,[16] comparisons must involve only isolated oxaphosphetanes.

The reaction shown in eq 5 probably proceeds via the formation of a MoOWC dimetallacyclobutane intermediate. The fact that the reaction proceeds to completion is not unexpected, since only a 3–4 kcal mol^{-1} for $\Delta G°_{rxn}$ is required, a relatively small quantity compared to the likely large energies of the bonds involved. A related alkylidene transfer between high oxidation state metal centers (Ta to W) has been reported previously.[17] Disproportionation of $M(O)(NAr)(O\text{-}t\text{-Bu})_2$ to $M(NAr)_2(O\text{-}t\text{-}Bu)_2$ (and presumably initially $MoO_2(O\text{-}t\text{-Bu})_2$ probably proceeds via a MOMN metallacycle.

So far we have concentrated on the analogy between loss of an olefin from 2-oxametallacycles and loss of an olefin from all-carbon metallacyclobutane complexes. An interesting question is whether the analogy holds to the extent that a π-bound aldehyde is required when it adds to an alkylidene. Little is known at this stage. In this context it is interesting to note that the rate of reaction of Ph_FCHO with **1b** to give **2b** is approximately three times the rate of reaction of Ph_FCHO with **1a** to give **2a**, and it is known that 2,3-bis(trifluoromethyl)norbornadiene reacts 2.5 times more rapidly with **1b** than with **1a**.[11] These data could be used as evidence that the mechanism of addition of a carbonyl group to an alkylidene is closely related to the mechanism of addition of an olefin to an alkylidene and therefore that π bonding of the aldehyde substrate is required to form a 2-oxametallacyclobutane complex. These and related questions concerning the details of the mechanism of reactions involving the carbonyl group and an alkylidene will be addressed in future investigations.

Experimental Section

(13) Observation of cis-WC_3 metallacycles was claimed[13a] in ring-opening metathesis reactions involving norbornenes, but later they were postulated to be diastereomeric trans isomers on the basis of NOE experiments.[13b] (a) Kress, J.; Osborn, J. A.; Greene, R. M. E.; Ivin, K. J.; Rooney, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 899. (b) Kress, J.; Osborn, J. A.; Ivin, K. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1234.
(14) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907.
(15) Haque, U. M.; Caughlan, C. N.; Ramirez, F.; Pilot, J. F.; Smith, C. P. *J. Am. Chem. Soc.* **1971**, *93*, 5229.

(16) (a) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863. (b) Vedeja, E.; Marth, C. F. *J. Am. Chem. Soc.* **1990**, *112*, 3905.
(17) Wengrovious, J. H.; Schrock, R. R. *Organometallics* **1982**, *1*, 148.

Mo(CH-*t*-Bu)(NAr)(O-t-Bu)$_2$ (150 mg, 3.07 × 10^{-4} mol) in octane (500 µL). The solution was kept at -40 °C for approximately 48 h to give the product as bright orange crystals (96 mg, 46%) suitable for X-ray analysis: ^{1}H NMR (toluene-d_8, 263 K) δ 6.96 (m, 3, H$_{Ar}$), 6.62 (d, 1, J_{HH} = 8.5, C$_\beta$), 4.41 (sept, 2, CHMe$_2$), 2.45 (d, 1, J_{HH} = 8.5), 1.55 (s, 9, OCMe$_3$), 1.45 (s, 9, OCMe$_3$), 1.38 (d, 6, CHMe$_2$), 1.32 (d, 6, CHMe$_2$), 1.08 (s, 9, CHCMe$_3$); ^{13}C (125.7 MHz, toluene-d_8, 250 K) δ 152.5 (C$_i$ or C$_o$ (NAr)), 147.3 (C$_i$ or C$_p$ (NAr)), 140.0 (CF, J_{CF} = 251), 137.5 (CF, J_{CF} = 245), 128.36 (C$_m$ (NAr)), 122.1 (CF, J_{CF} could not be determined due to overlap), (C$_i$ in CC$_6$F$_5$ could not be found), 84.82 (OCMe$_3$), 84.60 (OCMe$_3$), 72.53 (C$_\beta$, J_{CF} = 4, J_{CH} = 147), 69.98 (C$_\alpha$, J_{CH} = 127), 31.51 (OCMe$_3$), 30.72 (CHMe$_2$), 27.97 (CHCMe$_3$), 23.52 (CHCMe$_3$). The complex was not stable enough for elemental analysis.

Observation of *cis*-Mo[CH(*t*-Bu)CH(C$_6$F$_5$)O](NAr)(O-*t*-Bu)$_2$ (2a-cis). The metallacycle could be observed as a minor product (6%) from the reaction of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (15 mg, 3.1 × 10^{-4} mol) in C$_6$D$_6$ (350 µL) and pentafluorobenzaldehyde (9 mg, 4.6 × 10^{-4} mol) in C$_6$D$_6$ (350 µL). The sample was immediately frozen after addition of the aldehyde to 1a until the spectrum was taken. The major product for this reaction is 2a-trans (94%). ^{1}H NMR for 2a-cis: δ 6.95 (m, 3, H$_{Ar}$), 6.82 (d, 1, H$_\beta$), 2.64 (d, 1, H$_\alpha$, $J_{H_\alpha H_\beta}$ = 8), 1.57 (s, 9, OCCMe$_3$), 1.38 (s, 9, OCMe$_3$), CHMe$_2$ nor CHMe$_2$ could not be located, 1.09 (s, 9, CHCMe$_3$).

Rate of Decomposition of *trans*-Mo[CH(*t*-Bu)CH(C$_6$F$_5$)O](NAr)(O-*t*-Bu)$_2$. A solution of pure 2a-trans (45 mg, 6.6 × 10^{-5} mol) and mesitylene (~6 mg, 5 × 10^{-5} mol, internal standard) in C$_6$D$_6$ (3.00 mL) was split into 4 × 750 µL portions and loaded into 5-mm NMR tubes. The solutions were frozen in liquid N$_2$. First-order behavior was observed by monitoring the disappearance of the metallacycle β resonances versus the internal standard. Rates were determined at four different temperatures over a 30 °C range (35.1, 30.0, 25.0, 15.1 °C) with a sample equilibration time in the NMR probe of 10–15 min. Observed rate constants were 6.71, 4.72, 2.52, and 0.894 × 10^{-4} s^{-1}, respectively. The Arrhenius plot had ρ = 0.995. ^{1}H NMR for *trans*-(*t*-Bu)CHCH(C$_6$F$_5$) δ 6.44 (d, 1, olefinic, J_{HH} = 17), 6.03 (d, 1 olefinic, J_{HH} = 17), 0.94 (s, 9, CMe$_3$). ^{19}F NMR: δ 144.4 (F$_m$), 159.1 (F$_p$), 164.2 (F$_o$).

Rate of Decomposition of *trans*-W[CH(*t*-Bu)CH(C$_6$F$_5$)O](NAr)(O-*t*-Bu)$_2$ (2b-trans). The metallacycle was made in situ [W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (45 mg, 7.02 × 10^{-5} mol) and mesitylene (~10 mg, 8.3 × 10^{-5} mol) in C$_6$D$_6$ (1500 µL), C$_6$F$_5$CHO (20 mg, 1.01 × 10^{-4} mol, 1.3 equiv) in C$_6$D$_6$ (750 µL), 10 min at 22 °C]. The resulting solution was divided into 3 × 750 µL portions. The rates of metallacycle breakup were determined by monitoring the disappearance of the β proton versus the internal standard. First-order behavior was observed at three different temperatures (15.0, 25.1, 35.1 °C) with a sample equilibration time in the NMR probe of 10–15 min. Observed rate constants were

0.334, 1.11, and 3.82 × 10^{-4} s^{-1}, respectively. The Arrhenius plot had ρ = 0.999. ^{1}H NMR of 2b-trans: δ 7.04 (d, 2, H$_m$), 6.96 (t, 1, C$_p$), 6.53 (d, 1, H$_\beta$), 4.15 (septet, 2, CHMe$_2$), 2.27 (d, 1 H$_\alpha$, $J_{H_\alpha H_\beta}$ = 8), 1.46 (s, 9, OCMe$_3$), 1.41 (s, 9, OCMe$_3$), 1.40 (d, 6, CHMe$_2$), 1.34 (d, 6, CHMe$_2$), 1.08 (s, 9, CHCMe$_3$).

Rate of Decomposition of *cis*-W[CH(*t*-Bu)CH(C$_6$F$_5$)O](NAr)(O-*t*-Bu)$_2$ (2b-cis). The sample was made in a fashion similar to the method described above except that toluene-d_8 was used as solvent. First-order behavior was observed at 5 °C (7.6 × 10^{-4} s^{-1}) by monitoring the appearance of the cis-olefin versus an internal standard. ^{1}H NMR for 2b-cis (toluene-d_8, 5 °C): δ 7.02 (m, 3, H$_{Ar}$), 6.95 (d, 1, H$_\beta$), 4.14 (b, 2, CHMe$_2$), 3.05 (d, 1, H$_\alpha$, $J_{H_\alpha H_\beta}$ = 7.5), 1.51 (s, 9, OCMe$_3$), 1.46 (s, 9, OCMe$_3$), resonances for CHMe$_2$ could not be found probably due to overlap with 2b-trans, 1.03 (s, 9, CHCMe$_3$). ^{1}H NMR for *cis*-(*t*-Bu)CHCH-(C$_6$F$_5$): δ 5.64 (d, 1, J_{HH} = 12, (*t*-Bu)CHCH(C$_6$F$_5$)), 5.41 (d, 1, slightly broad, J_{HH} = 11, (t-Bu)CHCH(C$_6$F$_5$)), 0.77 (s, 9, CMe$_3$). ^{19}F NMR: δ 152.4 (F$_m$), 157.4 (F$_p$), 162.4 (F$_o$).

X-ray Crystal Structure of *trans*-Mo[CH(*t*-Bu)CH-(C$_6$F$_5$)O](NAr)(O-*t*-Bu)$_2$ (2a-trans). Data were collected at -72 °C on a Rigaku AFC6R diffractometer equipped with a liquid-nitrogen low-temperature device and using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) and a 12-kW rotating anode generator. A total of 8469 reflections were collected, 8219 of which were unique. Equivalent reflections were merged. The intensities of two representative reflections, which were measured after every 150 reflections, remained constant throughout data collection, indicating crystal and electronic stability. The structure was solved by direct methods.[18] Refinement was by full-matrix least squares methods using the TEXSAN crystallographic package from Molecular Structure Corp. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions (d_{C-H} = 0.95 Å). Crystal data: a = 18.08 (1) Å, b = 10.471 (7) Å, c = 18.072 (4) Å, β = 96.26 (3)°, space group $P2_1/c$, Z = 4, M_r = 683.65, V = 3401 (3) Å^3, ρ(calcd) = 1.335 g cm^{-3}, µ = 4.31 cm^{-1}. Final R_1 = 0.040 and R_2 = 0.053.

Supplementary Material Available: For 2a-trans, a labeled ORTEP drawing and tables of final positional parameters and thermal parameters (5 pages); a listing of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

(18) (a) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42. (b) Beurskens, P. T. Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, 6525 Ed Nijmegen, The Netherlands.